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Electrochemical Properties of the Ionic Liquid 1-Ethyl-3-methylimidazolium Difluorophosphate as an Electrolyte for Electric Double-Layer Capacitors

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The electrochemical properties of 1-ethyl-3-methylimidazolium difluorophosphate (EMImPO2F2) ionic liquid have been investigated as an electrolyte for electric double-layer capacitors using activated carbon electrodes. A two-electrode cell test reveals that the capacitance of EMImPO2F2 is larger than that of a typical ionic liquid electrolyte EMImBF4. At a charging voltage of 2.5 V, the capacitance obtained for EMImPO2F2 is 49 F g−1, which is higher than that of EMImBF4, which may be caused by the lower anodic stability of PO2F2 compared to BF4. The ionization potential of PO2F2 calculated by quantum mechanical calculations to estimate its anodic stability and was compared with several anions used in typical electrolytes. The results indicate that the anodic stability of PO2F2 is similar to that of PF6 and lower than those of BF4 and PF5.

Experimental

Reagents.—The ionic liquid electrolyte EMImBF4 was purchased from Kanto Kagaku and dried under vacuum (<1 Pa) at 373 K for 2 days. The starting chloride EMImCl was prepared by the reaction of 1-methylimidazole (Aldrich Chemicals, purity >99%) and chloroethane (Wako Chemicals, purity >99%) and was distilled by recrystallization from acetonitrile by adding ethylacetate. The potassium salt KPO2F2 was prepared by the reaction of KPO, (Wako Chemicals) and KPF6 (Aldrich purity >99.5%). The difluorophosphate ionic liquid EMImPO2F2 was prepared by the reaction of EMImCl and KPO2F2 and was purified through the activated alumina column as described in the literature. Final drying was performed under vacuum (<1 Pa) at 373 K for 1 week. The Karl–Fischer measurements showed that the typical water contents in these ionic liquids were below 100 ppm.

Measurements.—An electrochemical measurement was performed at 298 K with the aid of an electrochemical measurement system HZ-3000 (Hokuto Denko). The electrochemical window was measured using a vitreous carbon working electrode and a Pt counter electrode. The reference electrode was made of silver wire immersed in EMImBF4, containing 0.05 M AgBF4 that was separated from the electrolyte by a window made of porous Vycor glass. The potential was referenced to the ferrocenium/ferrocene (Fc+/Fc) redox couple.

A two-electrode cell made of poly(tetrafluoroethylene) (PTFE) was used for the EDLC tests. A pair of activated carbon sheets with a diameter of 10 mm, a thickness of 0.5 mm, and a weight of 0.021 g, 85 wt% of activated carbon from phenol resin (surface area, 2050 m2 g−1, mean pore diameter, 2.14 nm, and total pore volume, 1.10 cm3 g−1), 10 wt% of PTFE, and 5 wt% of carbon black] were used as electrodes. The electrodes dried under vacuum at 453 K overnight were immersed in the electrolyte and degassed under vacuum before use. The PTFE filter (ADVANTEC H100A013A, 35 μm thickness and 13 mm diameter) was used as a separator. Vitreous carbon disks were used as current collectors. The test cell was charged to a given voltage and discharged at a constant current rate of 5 mA. The capacitance C (F g−1) was calculated from the discharge curve using the relationship C = i/t/V, where i is the current, t is the time, V is the voltage, and w is the total weight of a pair of disk electrodes.

Electronic structure calculations.—Geometries were optimized at the HF and B3LYP level of theory by using the aug-cc-pVQZ basis set. Molecular volumes were calculated using the Monte Carlo method as implemented in Gaussian 03.
Results and Discussion

Electric double-layer capacitance.—Table I summarizes the physical properties of EMImPO2F2 and EMImBF4 used in the current study. The melting point of EMImPO2F2 (280 K) is slightly lower than that of EMImBF4 (288 K), and the conductivity and viscosity of EMImPO2F2 are comparable to those of EMImBF4.42,46 Figure 2 shows the charge–discharge curves obtained for EMImPO2F2, together with those obtained for EMImBF4 for comparison. In the EMImPO2F2, the voltage increase in the charge curve becomes sluggish at a charging voltage of 3.0 V, and the deformation of the discharge curve becomes apparent at a charging voltage of 3.5 V. The charge and discharge curves for EMImPO2F2 at a charging voltage of 4.0 V are totally deformed. The deterioration of the electrolyte causes such behavior and results in the increase in the internal resistance, as shown in the increase in the IR drop. Figure 3 shows the voltage dependence of capacitance for the EDLC using internal resistance, as shown in the increase in the IR drop. Figure 3 shows the voltage dependence of capacitance for the EDLC using EMImPO2F2, together with that using EMImBF4 as the electrolyte for comparison. The charging voltage was increased from 1.0 to 4.0 V by a 0.1 V step. Overall, the capacitance of EMImPO2F2 exhibits a higher voltage dependence than that of EMImBF4, leading to the higher capacitance of EMImPO2F2 at the charging voltages above 1.5 V. Although the origin of this behavior is not clear, the asymmetric PO2F2 can change the orientation of the electrode at high voltages. The capacitance obtained for EMImPO2F2 is 49 F g⁻¹ and is higher than 44 F g⁻¹ for EMImBF4 when the cell is charged at 2.5 V. The capacitance of EDLCs using activated carbon electrodes and BF4⁻-based ionic liquids is usually higher than those using other ionic liquids such as PF6⁻ and N(SO2CF3)2⁻-based ones.8,11 The larger capacitance of EMImPO2F2 compared to that of EMImBF4 is considered to arise from the characteristics of PO2F2. The obvious difference between PO2F2 and BF4⁻ in terms of molecular geometry is their symmetry. The PO2F2 anion has a C2v symmetry with a dipole moment and a more negative charge on the oxygen atoms compared to the fluorine atoms, whereas the BF4⁻ has a higher symmetry of Td. Such a difference in molecular geometry may affect the structure of the electric double layer and may result in the different voltage dependence of capacitance. According to the quantum mechanical calculation at PBE1PBE/aug-cc-pVTZ, the molecular volume of PO2F2 (85 Å³) is between the two popular fluoro-complex anions used for ionic liquid electrolytes, BF4⁻ (74 Å³) and PF6⁻ (97 Å³) (Fig. 4). The size of PO2F2 may be another factor for its high capacitance. In the region above the charging voltage of 3.0 V, the capacitance of EMImPO2F2 is increased steeply, which is ascribed to the decomposition of the electrolyte, whereas the capacitance of EMImBF4 exhibits almost a linear increase in this region.

Figure 5 shows the capacitance and coulomb efficiency of the EDLCs using (a) EMImPO2F2 and (b) EMImBF4 as a function of cycle number, where the charging voltage was increased every 50th cycle by 0.5 V from 2.0 V to 3.5 V. The capacitance loss during the cycles at 2.0 and 2.5 V is quite small in both the cases of EMImPO2F2 and EMImBF4. The capacitance of EMImPO2F2 slightly decreases during the cycles at 3.0 V and significantly drops during the cycles at 3.5 V, whereas the capacitance of EMImBF4 is constant during the cycles at 3.0 V, and slightly decreases as the cycle proceeds at 3.5 V. The drop in the coulomb efficiency at the high charging voltage is more evident for EMImPO2F2 than that for EMImBF4. These results indicate the lower electrochemical stability

Table I. Physical and thermal properties of the ionic liquids in the current study.

<table>
<thead>
<tr>
<th></th>
<th>Tm (K)</th>
<th>ρ (g cm⁻³)</th>
<th>MV (cm³ mol⁻¹)</th>
<th>η (mPa s)</th>
<th>σ (mS cm⁻¹)</th>
<th>Λ (S cm² mol⁻¹)</th>
<th>C (F g⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMImPO2F2</td>
<td>280</td>
<td>1.31</td>
<td>161</td>
<td>35</td>
<td>12</td>
<td>1.9</td>
<td>49</td>
<td>34</td>
</tr>
<tr>
<td>EMImBF4</td>
<td>288 (194)</td>
<td>1.27</td>
<td>156</td>
<td>34</td>
<td>13</td>
<td>2.0</td>
<td>44</td>
<td>36</td>
</tr>
</tbody>
</table>

Tm: melting point, Tg: glass transition temperature, ρ: density at 298 K, MV: molar volume at 298 K, η: viscosity at 298 K, σ: ionic conductivity at 298 K, Λ: molar conductivity at 298 K, and C: capacitance obtained for the present EDLC cell at the charging voltage of 2.5 V.
of EMImPO$_2$F$_2$ compared to that of EMImBF$_4$ in the present EDLC cell. Although there may be several factors on this point including the reaction of the electrolyte and surface functional groups on the activated carbon electrode, the difference in the anodic stability is considered to be one of the possible reasons, as shown below.

Anodic stability of PO$_2$F$_2^-$/H$_2$O$_2$ — Figure 6 shows the comparison of the electrochemical stability between EMImPO$_2$F$_2$ and EMImBF$_4$ by using the linear sweep voltammetry of a vitreous carbon electrode. The voltammetric curves for the two ionic liquids completely overlap at the cathode limit ($-2.5$ V vs Fe$^+/\text{Fc}$, where the current density is $0.5$ mA cm$^{-2}$), suggesting the decomposition of the cationic species. The anode limit of EMImPO$_2$F$_2$ is lower than that of EMImBF$_4$ by $0.3$ V, which arises from the difference in the stability of the anions against oxidation. The anodic stability of typical anionic species for the electrolytes in the organic solvents and for the ionic liquid electrolytes was experimentally determined on a vitreous carbon electrode, although such anions are often intercalated into graphitized materials at lower potentials. Theoretical works to evaluate the anodic stability were performed by calculating the ionization potential of the anions.

The highest occupied molecular orbital energy ($E_{\text{HOMO}}$) is based on Koopmans’ theorem and is valid only at the HF level. The vertical ionization potential ($E_v$) is also used for this purpose and is calculated from the energy difference between the total energy of the anion and that of the neutral radical without geometry optimization (the same geometry as the optimized geometry for the corresponding anion) based on the Franck–Condon principle. These calculations provide the order of the anodic stability of the anions. Table II lists $E_{\text{HOMO}}$ at HF/aug-cc-pVTZ and $E_v$ at PBE1PBE/aug-cc-pVTZ calculated for PO$_2$F$_2^-$ with the values for PF$_6^-$, BF$_4^-$, and ClO$_4^-$ for
comparison. In both the methods, the ionization potentials obtained in this study increases in the order of PO2F2 < ClO4− < BF4−. The low stability of ClO4− against oxidation compared to the common inorganic fluorooanions was already pointed out in previous studies.38,43 The present calculations proved that the anodic stability of PO2F2 is similar to that of ClO4− and validated the lower breaking-up voltage of the EDLC using EMImPO2F2 than that using EMImBF4.

Conclusion

In this study, the performance of the EDLC using EMImPO2F2 was measured and compared with that using EMImBF4. The high capacitance observed for EMImPO2F2 is attractive in the practical use. The breaking-up voltage of the EDLC using EMImPO2F2 is lower than 3.0 V, which may be explained by the lower anodic stability of PO2F2 than the typical fluorocomplex anions such as BF4−.

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References